

FORM PTO-1390  
(REV. 11-2000)

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

Mo-6598/LeA 33,210

U.S. APPLICATION NO (If known, see 37 CFR 1.5)

To Be Assigned **09/936124**

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP00/02118

10 March 2000 (10.03.00)

16 March 1999 (16.03.99)

TITLE OF INVENTION ROSIN AMINE ANTI-FOULING AGENTS

APPLICANT(S) FOR DO/EO/US KUNISCH, Franz; KUGLER, Martin; BRAEKMAN, Jean Claude; PLEHIERS, Mark and FERRARI, Gabriele

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☐ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☐ Other items or information:

U.S. APPLICATION NO. (if known) <b>09/936124</b> To Be Assigned		INTERNATIONAL APPLICATION NO. <b>PCT/EP00/02118</b>		ATTORNEY'S DOCKET NUMBER <b>Mo-6598/LeA 33,210</b>	
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21. <input checked="" type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a) (2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... <b>\$1000.00</b>  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$860.00</b>  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$710.00</b>  International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(I)-(4) ..... <b>\$690.00</b>  International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... <b>\$100.00</b> <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>CALCULATIONS PTO USE ONLY</b>	
				\$	860.00
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	0.00
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	9 -20 =	0	<b>x \$18.00</b>	\$	0.00
Independent claims	5 -3 =	2	<b>x \$80.00</b>	\$	160.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				\$	0.00
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$	1,020.00
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	0.00
<b>SUBTOTAL =</b>				\$	1,020.00
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	0.00
<b>TOTAL NATIONAL FEE =</b>				\$	1,020.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). <b>\$40.00</b> per property +				\$	0.00
<b>TOTAL FEES ENCLOSED =</b>				\$	1,020.00
				<b>Amount to be refunded:</b>	\$
				<b>charged:</b>	\$

- a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 1,020.00 to cover the above fees.  
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card  
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



**00157**

PATENT TRADEMARK OFFICE

SIGNATURE

Diderico van Eyl

NAME

38,641

REGISTRATION NUMBER

PATENT APPLICATION  
Mo6598  
LeA 33,210

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

APPLICATION OF )  
 )  
FRANZ KUNISCH ET AL ) PCT/EP00/02118  
 )  
SERIAL NUMBER: TO BE ASSIGNED )  
 )  
FILED: HEREWITH )  
 )  
TITLE: ROSIN AMINE ANTI-FOULING )  
AGENTS )

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

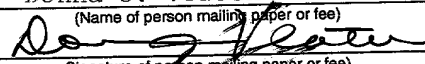
Please amend the subject patent application as follows:

"Express Mail" mailing label number ET146894121US  
Date of Deposit September 6, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

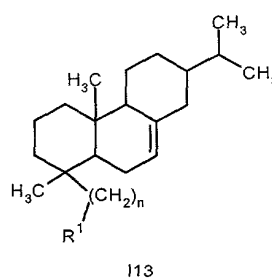
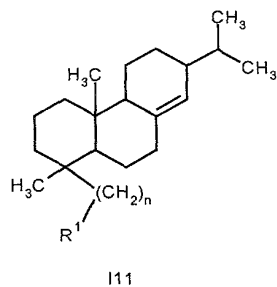
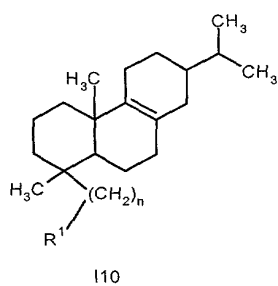
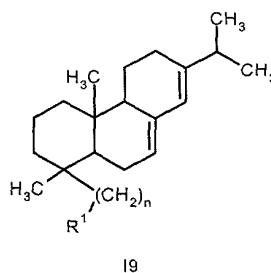
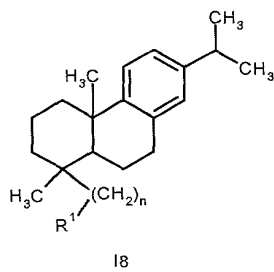
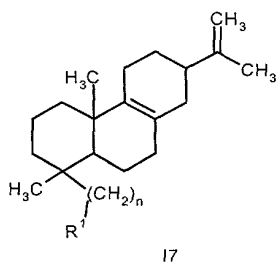
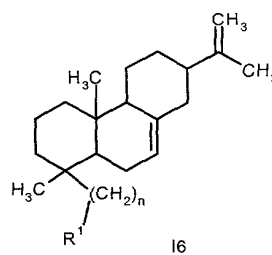
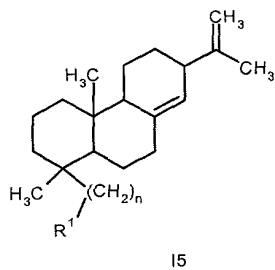
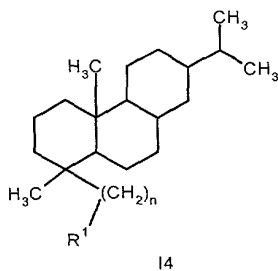
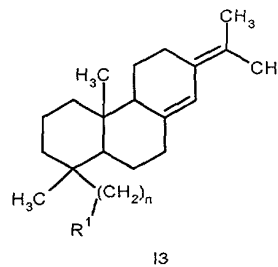
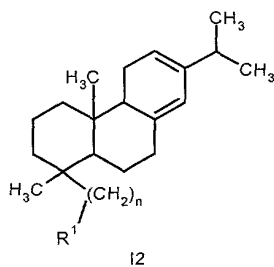
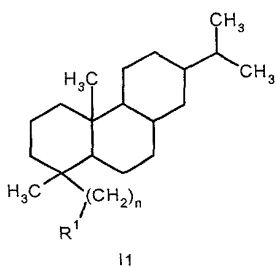
(Name of person mailing paper or fee)

  
Signature of person mailing paper or fee)

## IN THE CLAIMS

Please cancel Claims 1-7 and add new Claims 8-16:

--8. A compound selected from the group consisting of compounds having the formulae I1, I2, I3, I4, I5, I6, I7, I8, I9, I10, I11, I12, and I13:



wherein

R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup> wherein

R<sup>2</sup> represents a hydrogen atom or a C1 - C8-alkyl and

R<sup>3</sup> represents C=OR<sup>4</sup> wherein

R<sup>4</sup> represents a hydrogen atom or one of the groups OR<sup>5</sup> or NHR<sup>5</sup> wherein

R<sup>5</sup> designates a C1 - C8-alkyl or aryl, each optionally substituted by halogen; or

R<sup>1</sup> represents N=CR<sup>6</sup>R<sup>7</sup> wherein

R<sup>6</sup> represents a hydrogen atom or a C1 - C6-alkyl or aryl, and

R<sup>7</sup> represents a C1 - C6-alkyl or aryl, each optionally substituted by halogen; or

R<sup>1</sup> represents an isonitril, isocyanate, isothiocyanate or guanidino group; and

n represents 0 or 1.

9. The compound according to Claim 8, wherein R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup>, and wherein

R<sup>2</sup> represents a hydrogen atom or a C1 - C4-alkyl and

R<sup>3</sup> represents C=OR<sup>4</sup> wherein

R<sup>4</sup> represents a hydrogen atom or one of the groups OR<sup>5</sup> or NHR<sup>5</sup> wherein

R<sup>5</sup> represents a C1 - C4-alkyl or aryl, each optionally substituted by halogen; or

R<sup>1</sup> represents N=CR<sup>6</sup>R<sup>7</sup> wherein

R<sup>6</sup> represents a hydrogen atom, methyl or optionally halogen substituted aryl, and

R<sup>7</sup> represents a C1 - C4-alkyl or optionally halogen substituted aryl; or

R<sup>1</sup> represents an isonitrile, isocyanate, isothiocyanate or guanidino moiety.

10. The compound according to Claim 8, wherein

$R^1$  represents  $NR^2R^3$  wherein

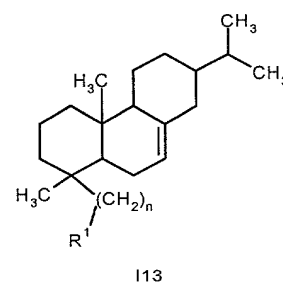
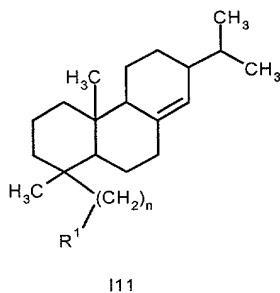
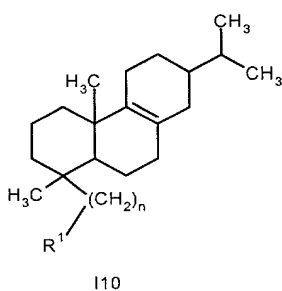
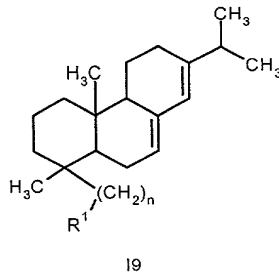
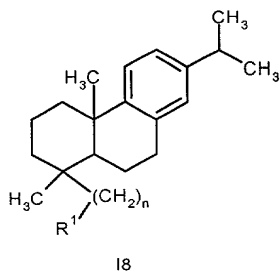
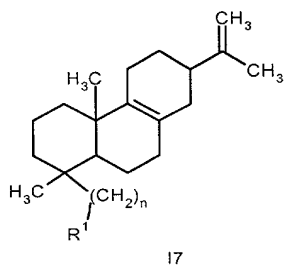
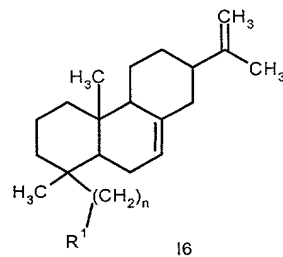
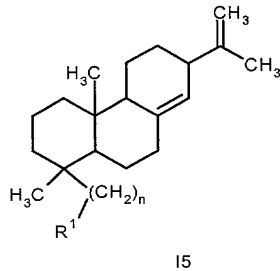
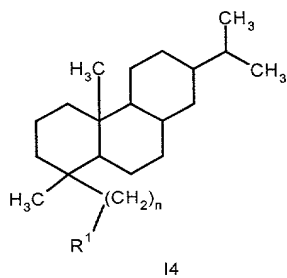
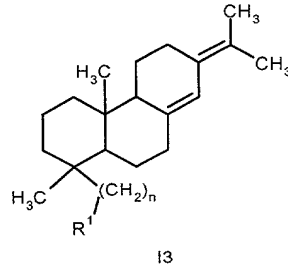
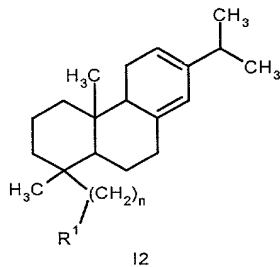
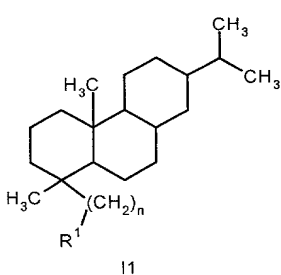
$R^2$  represents a hydrogen atom and

$R^3$  represents  $C=OR^4$  wherein

$R^4$  represents a hydrogen atom.

Mo6598

11. A method for controlling or combatting a marine or freshwater fouling organism comprising contacting said organism or the locus thereof with an anti-fouling-effective amount of at least one selected from the group consisting of compounds having the formulae I1, I2, I3, I4, I5, I6, I7, I8, I9, I10, I11, I12, and I13:



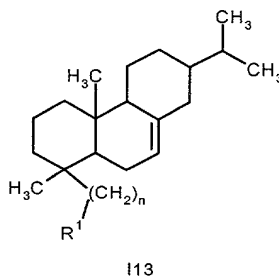
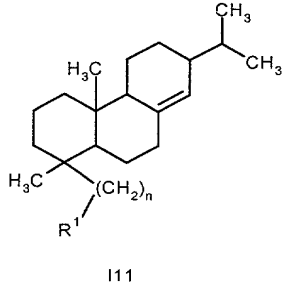
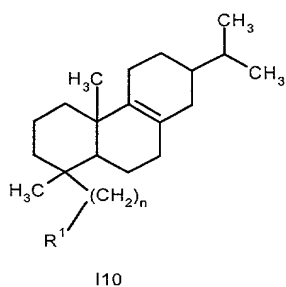
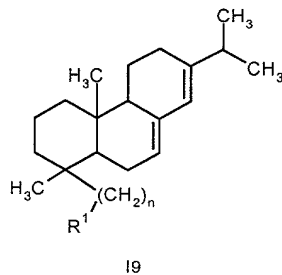
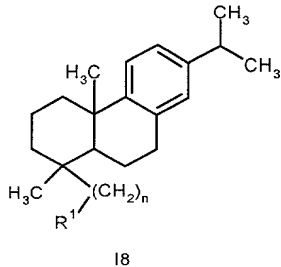
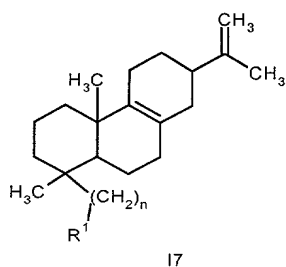
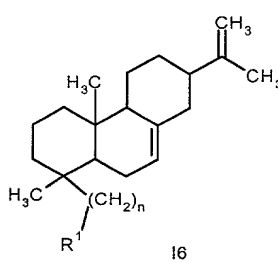
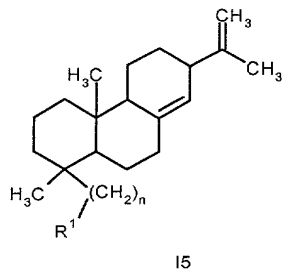
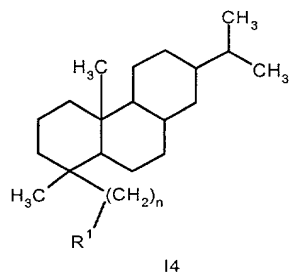
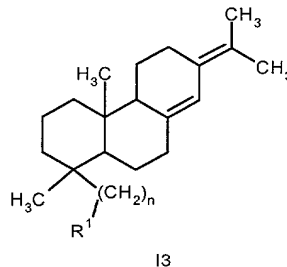
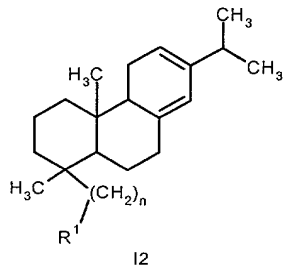
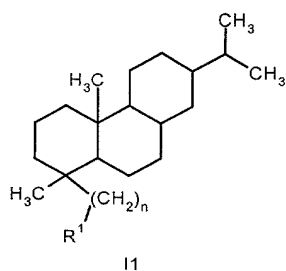
wherein

R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup> wherein

- $R^2$  represents a hydrogen atom or a C1 - C8-alkyl and  
 $R^3$  represents  $C=OR^4$  wherein  
 $R^4$  represents a hydrogen atom or one of the groups  $OR^5$  or  $NHR^5$   
 wherein  
 $R^5$  designates a C1 - C8-alkyl or aryl, each optionally substituted by  
 halogen; or  
 $R^1$  represents  $N=CR^6R^7$  wherein  
 $R^6$  represents a hydrogen atom or a C1 - C6-alkyl or aryl, and  
 $R^7$  represents a C1 - C6-alkyl or aryl, each optionally substituted by  
 halogen; or  
 $R^1$  represents an isonitril, isocyanate, isothiocyanate or guanidino group;  
 and  
 $n$  represents 0 or 1.



12. An agent comprising an antifouling-effective amount of at least one compound and an aquatically acceptable inert carrier, wherein the compound is selected from the group consisting of compounds having the formulae I1, I2, I3, I4, I5, I6, I7, I8, I9, I10, I11, I12, and I13:



wherein

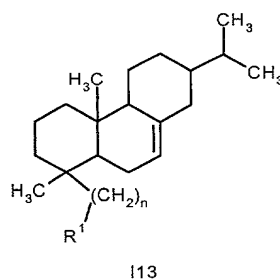
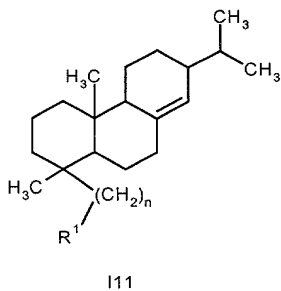
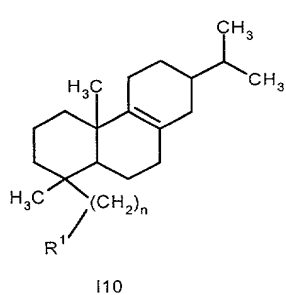
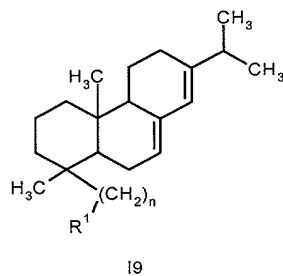
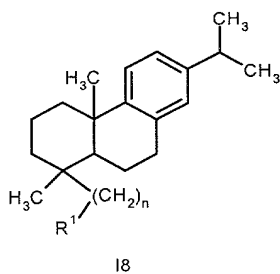
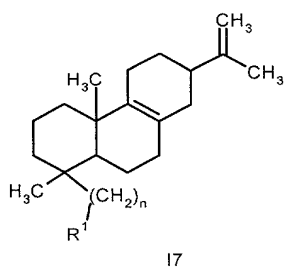
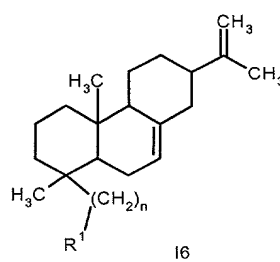
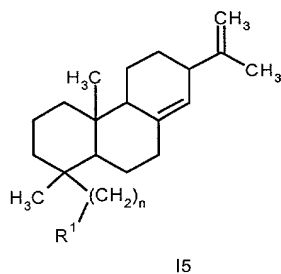
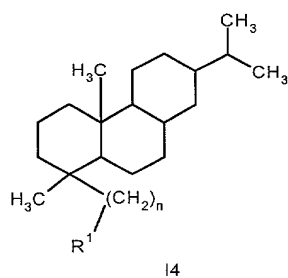
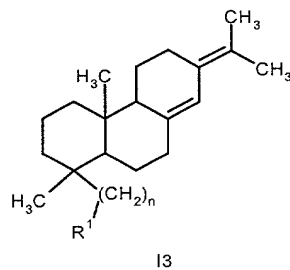
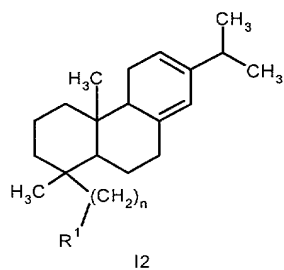
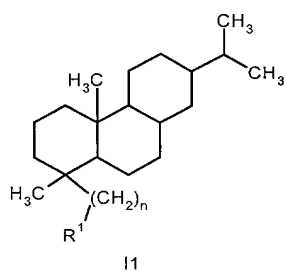
$R^1$  represents  $NR^2R^3$ , wherein

$R^2$  represents a hydrogen atom or a C1 - C8-alkyl and

- $R^3$  represents  $C=OR^4$  wherein
- $R^4$  represents a hydrogen atom or one of the groups  $OR^5$  or  $NHR^5$ , wherein
- $R^5$  designates a C1 - C8-alkyl or aryl, each optionally substituted by halogen; or
- $R^1$  represents  $N=CR^6R^7$  wherein
- $R^6$  represents a hydrogen atom or a C1 - C6-alkyl or aryl, and
- $R^7$  represents a C1 - C6-alkyl or aryl, each optionally substituted by halogen; or
- $R^1$  represents an isonitril, isocyanate, isothiocyanate or guanidino group; and
- $n$  represents 0 or 1.

13. A method for controlling and combatting a marine fouling organism, a freshwater fouling organism, or combinations thereof,

the method comprising treating the organism with a compound selected from the group consisting of compounds having the formulae I1, I2, I3, I4, I5, I6, I7, I8, I9, I10, I11, I12, and I13:



wherein

R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup> wherein

R<sup>2</sup> represents a hydrogen atom or a C1 - C8-alkyl and

R<sup>3</sup> represents C=OR<sup>4</sup> wherein

R<sup>4</sup> represents a hydrogen atom or one of the groups OR<sup>5</sup> or NHR<sup>5</sup> wherein

R<sup>5</sup> designates a C1 - C8-alkyl or aryl, each optionally substituted by halogen; or

R<sup>1</sup> represents N=CR<sup>6</sup>R<sup>7</sup> wherein

R<sup>6</sup> represents a hydrogen atom or a C1 - C6-alkyl or aryl, and

R<sup>7</sup> represents a C1 - C6-alkyl or aryl, each optionally substituted by halogen; or

R<sup>1</sup> represents an isonitril, isocyanate, isothiocyanate or guanidino group; and

n represents 0 or 1.

14. The composition according to Claim 8, wherein

R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup>, wherein

R<sup>2</sup> represents a hydrogen atom or a C1 - C4-alkyl and

R<sup>3</sup> represents C=OR<sup>4</sup> wherein

R<sup>4</sup> represents a hydrogen atom or one of the groups OR<sup>5</sup> or NHR<sup>5</sup> wherein

R<sup>5</sup> represents a C1 - C4-alkyl or aryl, each optionally substituted by halogen; or

R<sup>1</sup> represents N=CR<sup>6</sup>R<sup>7</sup> wherein

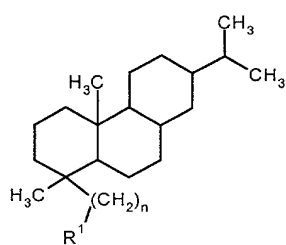
R<sup>6</sup> represents a hydrogen atom, methyl or optionally halogen substituted aryl, and

R<sup>7</sup> represents a C1 - C4-alkyl or optionally halogen substituted aryl; or

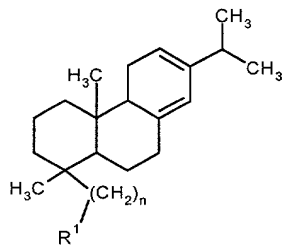
R<sup>1</sup> represents an isonitrile, isocyanate, isothiocyanate or guanidino moiety.

15. The method of Claim 13, wherein the organism is treated with an agent comprising an antifouling-effective amount of the compound and an aquatically acceptable inert carrier.

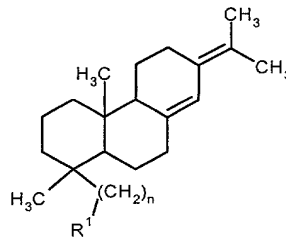
16. A process for preparing an anti-fouling agent comprising mixing a compound with an aquatically acceptable inert carrier, wherein the compound is selected from the group consisting of compounds having the formulae I1, I2, I3, I4, I5, I6, I7, I8, I9, I10, I11, I12, and I13:



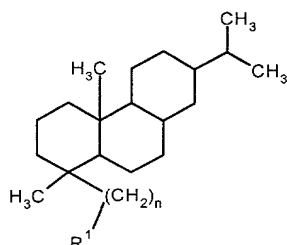
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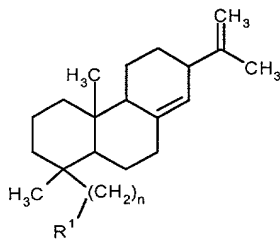
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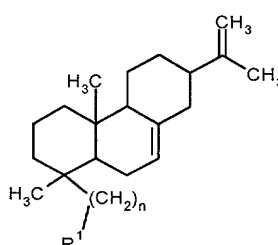
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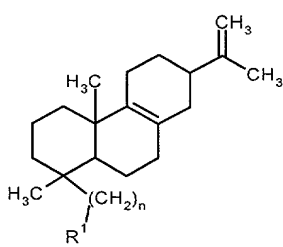
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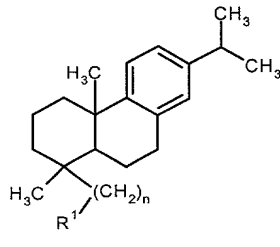
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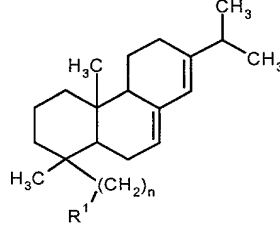
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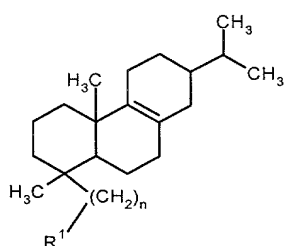
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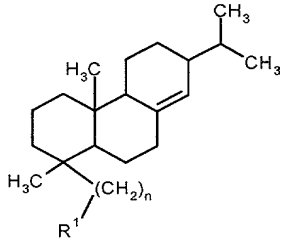
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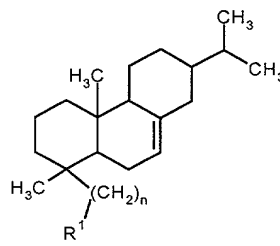
I9



I10



I11



I13

wherein

R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup> wherein

R<sup>2</sup> represents a hydrogen atom or a C1 - C8-alkyl and

R<sup>3</sup> represents C=OR<sup>4</sup> wherein

R<sup>4</sup> represents a hydrogen atom or one of the groups OR<sup>5</sup> or NHR<sup>5</sup>  
wherein

R<sup>5</sup> designates a C1 - C8-alkyl or aryl, each optionally substituted by  
halogen; or

R<sup>1</sup> represents N=CR<sup>6</sup>R<sup>7</sup> wherein

R<sup>6</sup> represents a hydrogen atom or a C1 - C6-alkyl or aryl, and

R<sup>7</sup> represents a C1 - C6-alkyl or aryl, each optionally substituted by  
halogen; or

R<sup>1</sup> represents an isonitril, isocyanate, isothiocyanate or guanidino group;  
and

n represents 0 or 1.--

IN THE SPECIFICATION

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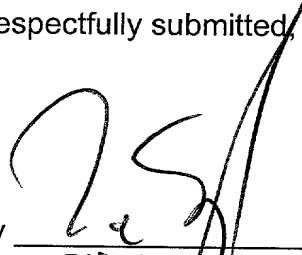
This application is the National Stage Application of WO 00/55117, which  
claims a priority from German Application 99 105349.7, filed March 16, 1999.

REMARKS

Entry of this Preliminary Amendment is requested. The above-made amendments have been made to place the application in conformance with American standards. No new matter has been added.

Respectfully submitted,

By



Diderico van Eyl  
Attorney for Applicants  
Reg. No. 38,641

Bayer Corporation  
100 Bayer Road  
Pittsburgh, Pennsylvania 15205-9741  
(412) 777-8355  
FACSIMILE PHONE NUMBER:  
(412) 777-8363

/jme/DVE0306

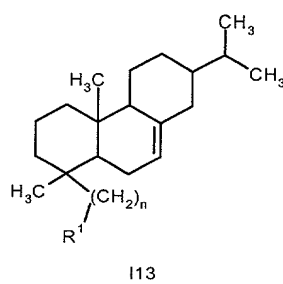
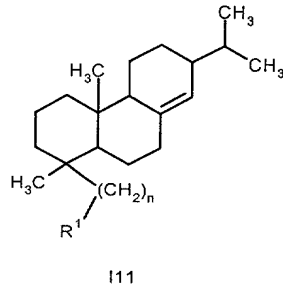
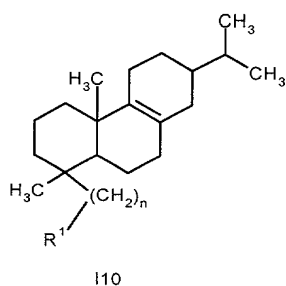
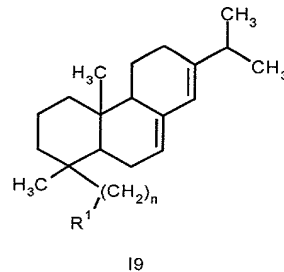
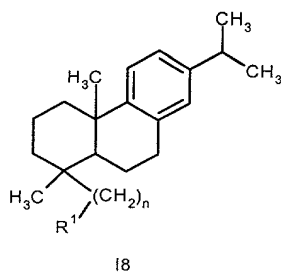
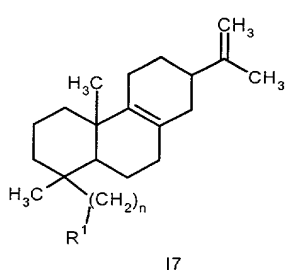
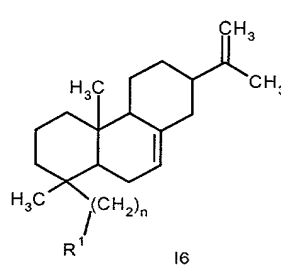
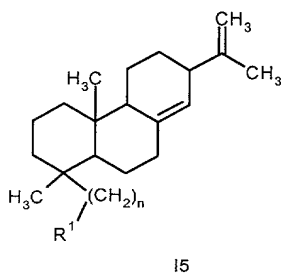
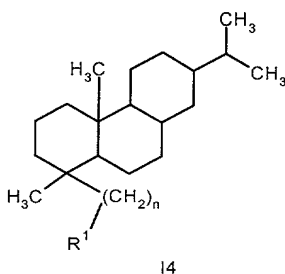
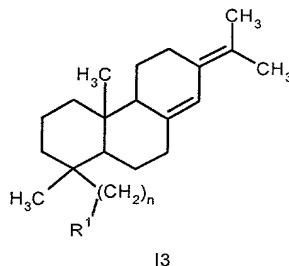
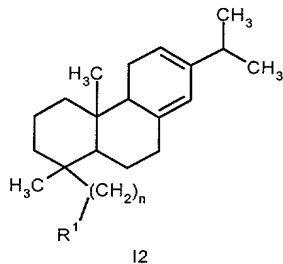
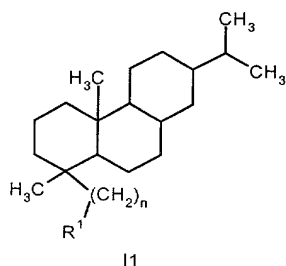
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Variable	Mean	SD	Min	Max
Age	35.2	12.5	18	65
Gender	0.45	0.50	0	1
Marital Status	0.60	0.49	0	1
Education	12.5	1.5	9	16
Income	3500	1500	1000	8000
Health Status	0.75	0.43	0	1
Exercise Frequency	2.5	1.5	0	5
Stress Level	4.5	1.5	1	7
Sleep Quality	3.5	1.5	1	5
Diet Quality	3.0	1.5	1	5
Work-Life Balance	3.5	1.5	1	5
Life Satisfaction	4.0	1.5	1	5
Overall Well-being	3.5	1.5	1	5

IN THE CLAIMS

Claims 1-7 were cancelled and new Claims 8-16 were added:

--8. A compound selected from the group consisting of compounds having the formulae I1, I2, I3, I4, I5, I6, I7, I8, I9, I10, I11, I12, and I13:





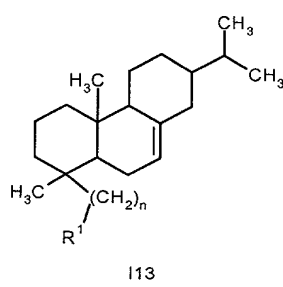
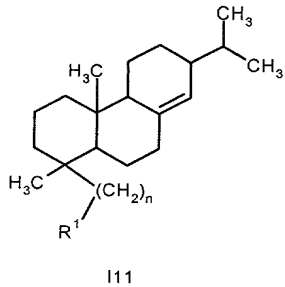
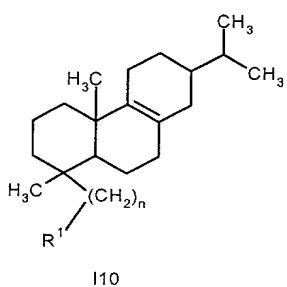
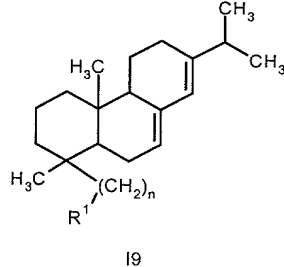
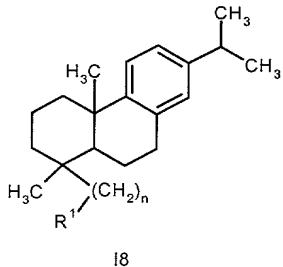
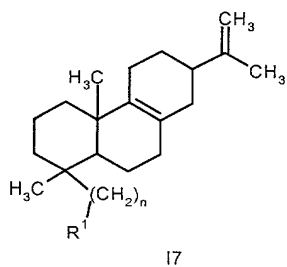
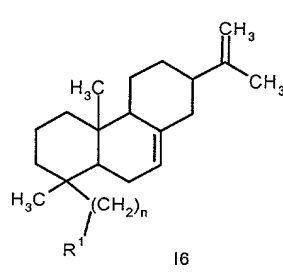
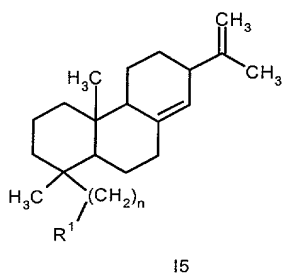
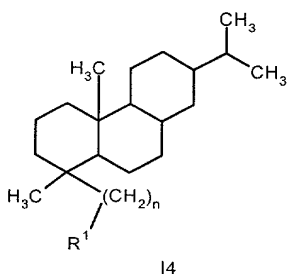
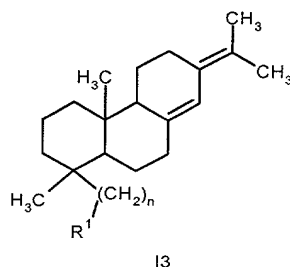
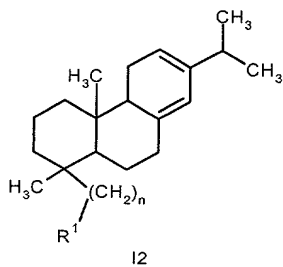
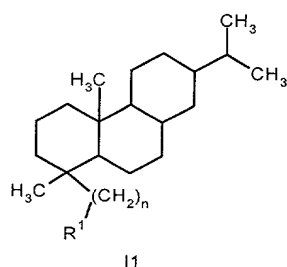
wherein

- R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup> wherein
- R<sup>2</sup> represents a hydrogen atom or a C1 - C8-alkyl and
- R<sup>3</sup> represents C=OR<sup>4</sup> wherein
- R<sup>4</sup> represents a hydrogen atom or one of the groups OR<sup>5</sup> or NHR<sup>5</sup> wherein
- R<sup>5</sup> designates a C1 - C8-alkyl or aryl, each optionally substituted by halogen; or
- R<sup>1</sup> represents N=CR<sup>6</sup>R<sup>7</sup> wherein
- R<sup>6</sup> represents a hydrogen atom or a C1 - C6-alkyl or aryl, and
- R<sup>7</sup> represents a C1 - C6-alkyl or aryl, each optionally substituted by halogen; or
- R<sup>1</sup> represents an isonitril, isocyanate, isothiocyanate or guanidino group; and
- n represents 0 or 1.
9. The compound according to Claim 8, wherein R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup>, and wherein
- R<sup>2</sup> represents a hydrogen atom or a C1 - C4-alkyl and
- R<sup>3</sup> represents C=OR<sup>4</sup> wherein
- R<sup>4</sup> represents a hydrogen atom or one of the groups OR<sup>5</sup> or NHR<sup>5</sup> wherein
- R<sup>5</sup> represents a C1 - C4-alkyl or aryl, each optionally substituted by halogen; or
- R<sup>1</sup> represents N=CR<sup>6</sup>R<sup>7</sup> wherein
- R<sup>6</sup> represents a hydrogen atom, methyl or optionally halogen substituted aryl, and
- R<sup>7</sup> represents a C1 - C4-alkyl or optionally halogen substituted aryl; or
- R<sup>1</sup> represents an isonitrile, isocyanate, isothiocyanate or guanidino moiety.
10. The compound according to Claim 8, wherein

- $R^1$  represents  $NR^2R^3$  wherein  
 $R^2$  represents a hydrogen atom and  
 $R^3$  represents  $C=OR^4$  wherein  
 $R^4$  represents a hydrogen atom.

2020-04-23-09:00

11. A method for controlling or combatting a marine or freshwater fouling organism comprising contacting said organism or the locus thereof with an anti-fouling-effective amount of at least one selected from the group consisting of compounds having the formulae I1, I2, I3, I4, I5, I6, I7, I8, I9, I10, I11, I12, and I13:

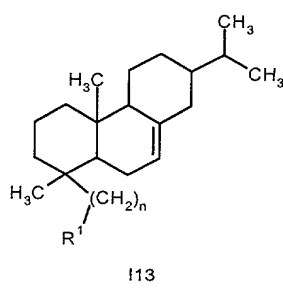
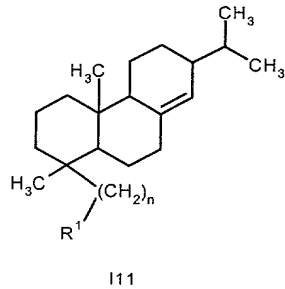
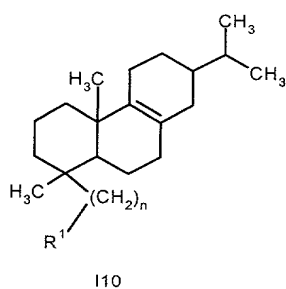
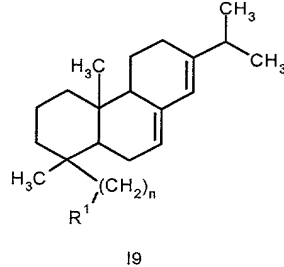
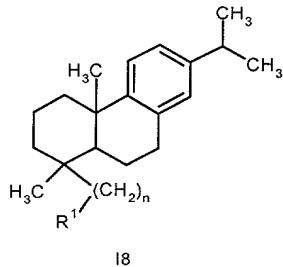
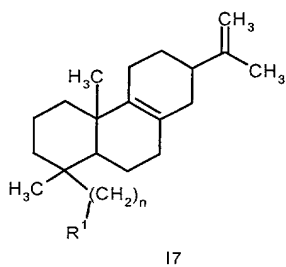
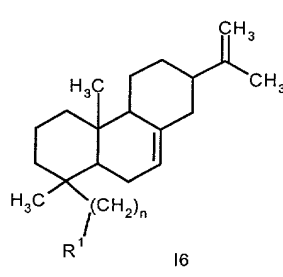
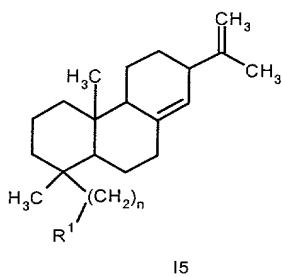
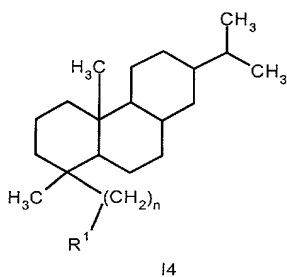
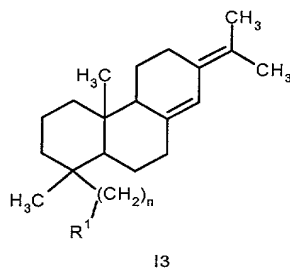
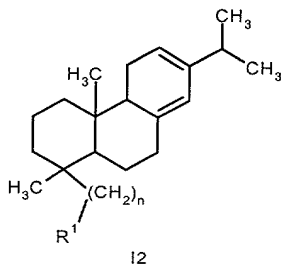
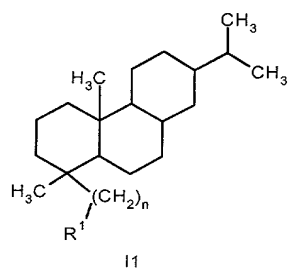


wherein

R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup> wherein

- $R^2$  represents a hydrogen atom or a C1 - C8-alkyl and  
 $R^3$  represents  $C=OR^4$  wherein  
 $R^4$  represents a hydrogen atom or one of the groups  $OR^5$  or  $NHR^5$  wherein  
 $R^5$  designates a C1 - C8-alkyl or aryl, each optionally substituted by halogen; or  
 $R^1$  represents  $N=CR^6R^7$  wherein  
 $R^6$  represents a hydrogen atom or a C1 - C6-alkyl or aryl, and  
 $R^7$  represents a C1 - C6-alkyl or aryl, each optionally substituted by halogen; or  
 $R^1$  represents an isonitril, isocyanate, isothiocyanate or guanidino group; and  
 $n$  represents 0 or 1.

12. An agent comprising an antifouling-effective amount of at least one compound and an aquatically acceptable inert carrier, wherein the compound is selected from the group consisting of compounds having the formulae I1, I2, I3, I4, I5, I6, I7, I8, I9, I10, I11, I12, and I13:



wherein

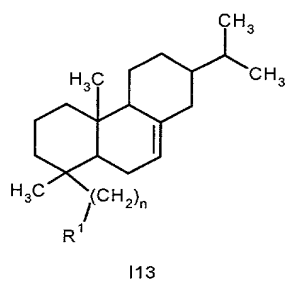
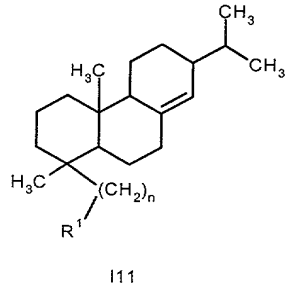
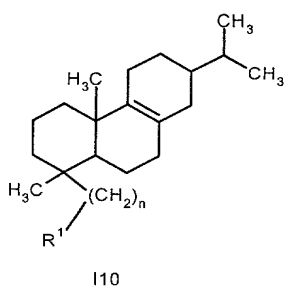
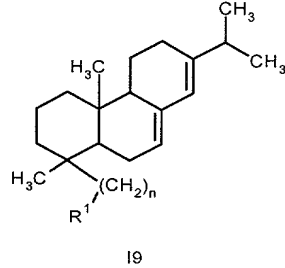
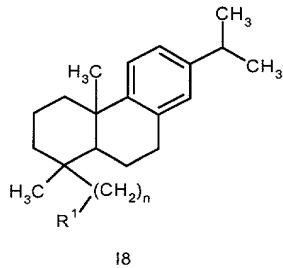
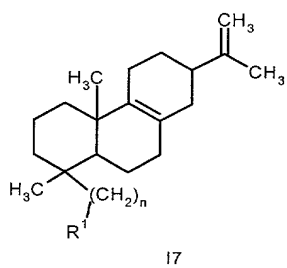
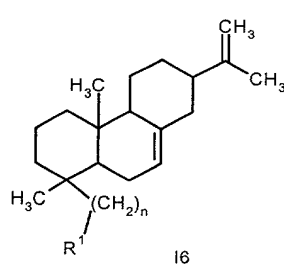
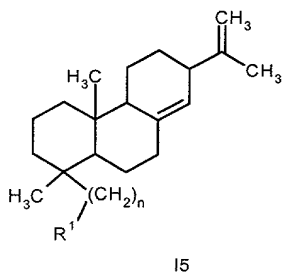
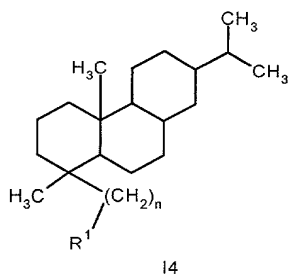
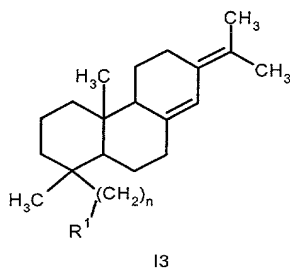
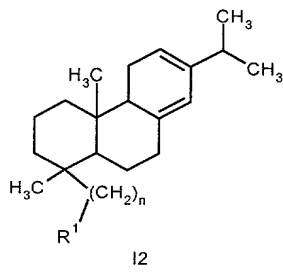
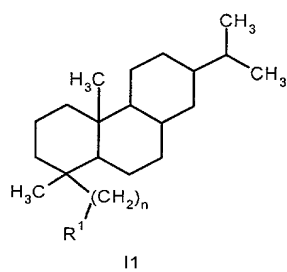
$R^1$  represents  $NR^2R^3$ , wherein

$R^2$  represents a hydrogen atom or a C1 - C8-alkyl and

- $R^3$  represents  $C=OR^4$  wherein  
 $R^4$  represents a hydrogen atom or one of the groups  $OR^5$  or  $NHR^5$ ,  
 wherein  
 $R^5$  designates a C1 - C8-alkyl or aryl, each optionally substituted by  
 halogen; or  
 $R^1$  represents  $N=CR^6R^7$  wherein  
 $R^6$  represents a hydrogen atom or a C1 - C6-alkyl or aryl, and  
 $R^7$  represents a C1 - C6-alkyl or aryl, each optionally substituted by  
 halogen; or  
 $R^1$  represents an isonitril, isocyanate, isothiocyanate or guanidino group;  
 and  
 n represents 0 or 1.

13. A method for controlling and combatting a marine fouling organism, a freshwater fouling organism, or combinations thereof,

the method comprising treating the organism with a compound selected from the group consisting of compounds having the formulae I1, I2, I3, I4, I5, I6, I7, I8, I9, I10, I11, I12, and I13:



wherein

R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup> wherein

R<sup>2</sup> represents a hydrogen atom or a C1 - C8-alkyl and

R<sup>3</sup> represents C=OR<sup>4</sup> wherein

R<sup>4</sup> represents a hydrogen atom or one of the groups OR<sup>5</sup> or NHR<sup>5</sup> wherein

R<sup>5</sup> designates a C1 - C8-alkyl or aryl, each optionally substituted by halogen; or

R<sup>1</sup> represents N=CR<sup>6</sup>R<sup>7</sup> wherein

R<sup>6</sup> represents a hydrogen atom or a C1 - C6-alkyl or aryl, and

R<sup>7</sup> represents a C1 - C6-alkyl or aryl, each optionally substituted by halogen; or

R<sup>1</sup> represents an isonitril, isocyanate, isothiocyanate or guanidino group; and

n represents 0 or 1.

14. The composition according to Claim 8, wherein

R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup>, wherein

R<sup>2</sup> represents a hydrogen atom or a C1 - C4-alkyl and

R<sup>3</sup> represents C=OR<sup>4</sup> wherein

R<sup>4</sup> represents a hydrogen atom or one of the groups OR<sup>5</sup> or NHR<sup>5</sup> wherein

R<sup>5</sup> represents a C1 - C4-alkyl or aryl, each optionally substituted by halogen; or

R<sup>1</sup> represents N=CR<sup>6</sup>R<sup>7</sup> wherein

R<sup>6</sup> represents a hydrogen atom, methyl or optionally halogen substituted aryl, and

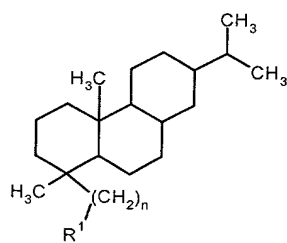
R<sup>7</sup> represents a C1 - C4-alkyl or optionally halogen substituted aryl; or

R<sup>1</sup> represents an isonitrile, isocyanate, isothiocyanate or guanidino moiety.

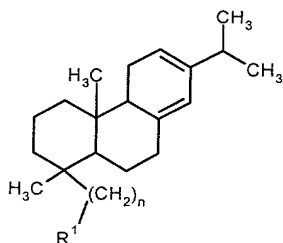


15. The method of Claim 13, wherein the organism is treated with an agent comprising an antifouling-effective amount of the compound and an aquatically acceptable inert carrier.

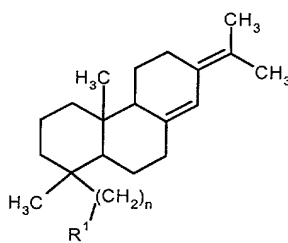
16. A process for preparing an anti-fouling agent comprising mixing a compound with an aquatically acceptable inert carrier, wherein the compound is selected from the group consisting of compounds having the formulae I1, I2, I3, I4, I5, I6, I7, I8, I9, I10, I11, I12, and I13:



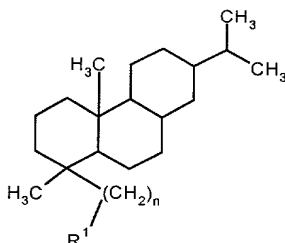
I1



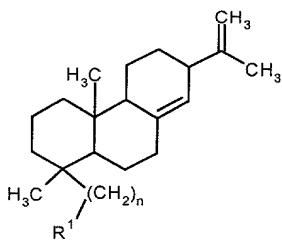
I2



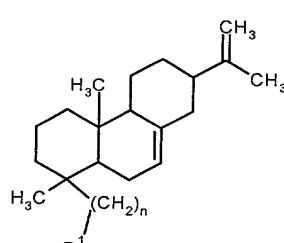
I3



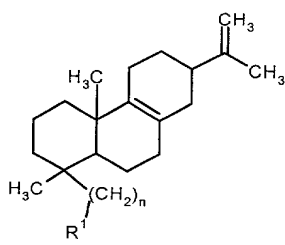
I4



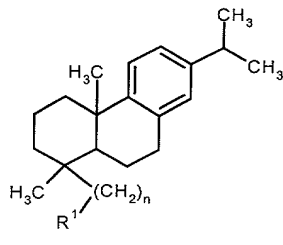
I5



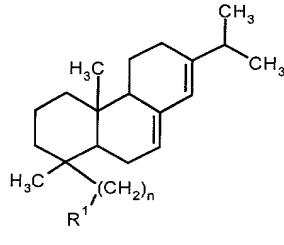
I6



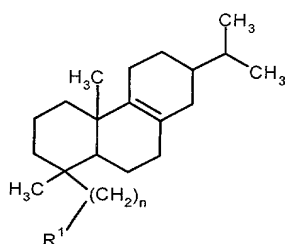
I7



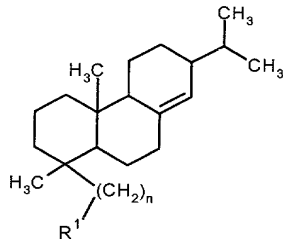
I8



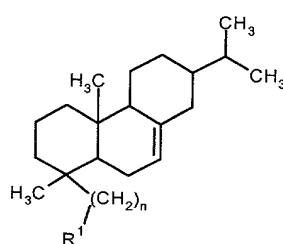
I9



I10



I11



I13

wherein

R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup> wherein

R<sup>2</sup> represents a hydrogen atom or a C1 - C8-alkyl and

R<sup>3</sup> represents C=OR<sup>4</sup> wherein

R<sup>4</sup> represents a hydrogen atom or one of the groups OR<sup>5</sup> or NHR<sup>5</sup> wherein

R<sup>5</sup> designates a C1 - C8-alkyl or aryl, each optionally substituted by halogen; or

R<sup>1</sup> represents N=CR<sup>6</sup>R<sup>7</sup> wherein

R<sup>6</sup> represents a hydrogen atom or a C1 - C6-alkyl or aryl, and

R<sup>7</sup> represents a C1 - C6-alkyl or aryl, each optionally substituted by halogen; or

R<sup>1</sup> represents an isonitril, isocyanate, isothiocyanate or guanidino group; and

n represents 0 or 1.--

#### IN THE SPECIFICATION

On page 1, below the title, the following was added:

This application is the National Stage Application of WO 00/55117, which claims a priority from German Application 99 105349.7, filed March 16, 1999.

**Rosin Amine Anti-Fouling Agents****Field of invention**

5 The invention relates to new and known compounds as well as methods for preventing the attachment of aquatic organisms to surfaces which are submerged for extensive periods of time in water. More particularly, this invention relates to the protection of submerged surfaces with new isonitrile, formamide, isocyanate and isothiocyanate anti-fouling agents.

**Background of the invention**

10 The ever recurring growth of fouling organisms on underwater structures such as ships, docks, piers, pilings, fishnets, heat exchangers, dams, piping structures, intake screens, cooling towers and the like is a costly and hazardous problem in both marine and freshwater endeavors. The presence of fouling organisms such as barnacles, zebra mussels, algae, diatoms, hydroids, bryozoa, ascidians, tubeworms, Asiatic  
15 clams and the like causes economic damage in various ways: for example, attachment to the hulls of ships reduces fuel efficiency and causes loss of profitable sailing time because of the need to clean the hulls. Similarly, the attachment of these organisms to cooling water equipment decreases heat conductivity which eventually  
20 reduces or block the cooling power of the equipment and drives up cost.

A variety of agents useful for controlling fouling organisms in fresh water or sea water have been used to prevent the attachment and overgrowth of these organisms.

25 A common method of controlling the presence or attachment of fouling organisms is to coat or permeate the underwater structure with a composition which comprises mixtures of toxic compounds such as tri-n-butyl tin or copper compounds. Anti-fouling agents in the form of a paint can contain up to 60% by weight of the active ingredients and can be used to paint surfaces such as the hull of ships. The paint  
30 prevents attachment and growth of fouling organisms by continuously releasing anti-fouling agents underwater. The disadvantage of many of the present anti-fouling

- 2 -

agents is that they are persistent in the environment, are often acutely toxic and degrade too slowly in aquatic environments and are, therefore, ecologically harmful. Hazardous anti-fouling agents can eventually bioaccumulate and enter the food chain and therefore represent a threat to marine and human life.

5

For example, it is well established that heavy metal compounds, especially organotin compounds that are widely used as anti-fouling agents, accumulate in mussels.

It is an object of this invention to provide an environmentally and ecologically sound method of combatting or controlling marine and freshwater fouling organisms.

10

It is another object of this invention to provide an effective method for protecting aquatic structures against fouling by marine or freshwater fouling organisms.

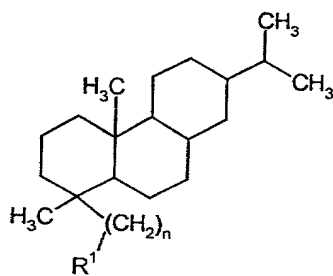
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It is a further object of this invention to provide antifoulant compositions which comprises certain derivatives of rosin compounds as the active agents.

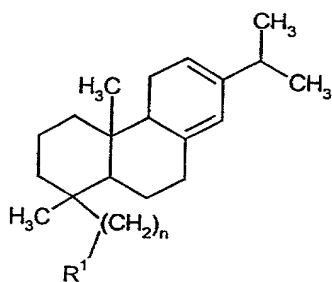
### Summary of the Invention

The present invention provides new and known compounds and a method to prevent settlement on surfaces by marine or freshwater fouling organism which comprises contacting said organism or the locus thereof with an anti-fouling-effective amount of at least one compound of formula I1-I13

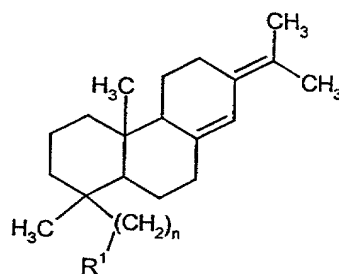
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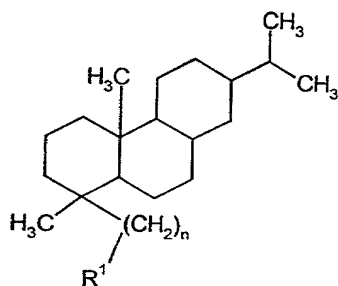
I1



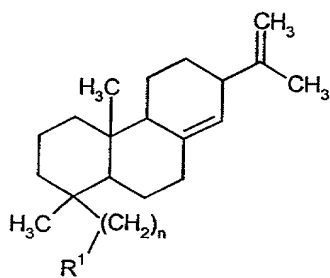
I2



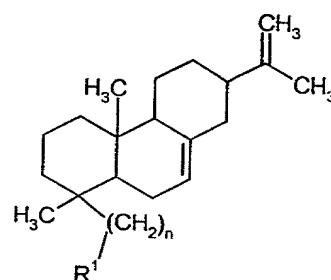
I3



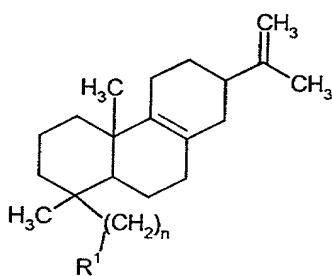
I4



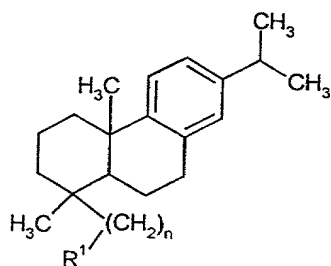
I5



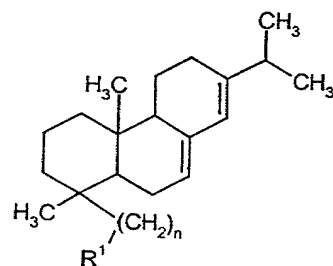
I6



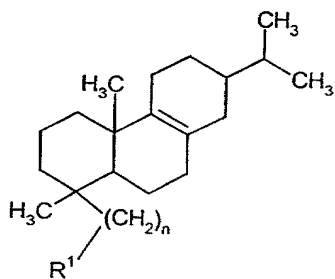
I7



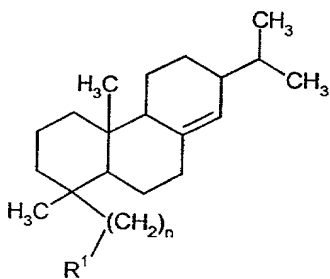
I8



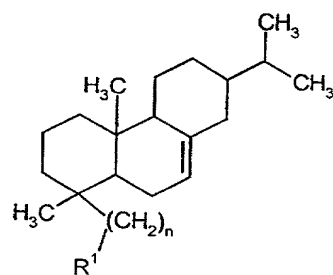
I9



I10



I11



I13

formula I1 -I13

wherein

$R^1$  represents  $NR^2R^3$  wherein

$R^2$  represents a hydrogen atom, C1 - C8-alkyl and

$R^3$  represents  $C=OR^4$  wherein

$R^4$  represents a hydrogen atom or one of the groups  $OR^5$  or  $NHR^5$  wherein

$R^5$  designates C1 - C8-alkyl or aryl, each optionally substituted by halogen; or

$R^1$  represents  $N=CR^6R^7$  wherein

$R^6$  represents a hydrogen atom, C1 - C6-alkyl or aryl, and

$R^7$  represents C1 - C6-alkyl or aryl, each optionally substituted by halogen; or

$R^1$  represents an isonitrile, isocyanate, isothiocyanate or a guanidino group; and

$n$  represents 0 or 1.

In the specification and claims the term:

halogen has the meaning of Cl, Br, I or F;

alkyl has the meaning of straight-chain or branched alkyl with 1 to 8, preferably 1 to 4 carbon atoms;

aryl has the meaning of aromatic, mono- or polycyclic hydrocarbon rings such as for example and preferred: naphthyl, anthranyl, phenanthryl, especially phenyl.

Preferred are compounds of formula I1 - I13 wherein

$R^1$  represents  $NR^2R^3$  wherein

$R^2$  represents a hydrogen atom or C1 - C4-alkyl and

$R^3$  represents  $C=OR^4$  wherein

$R^4$  represents a hydrogen atom or one of the groups  $OR^5$  or  $NHR^5$  wherein

$R^5$  represents C1 - C4-alkyl or aryl, each optionally substituted by halogen; or

$R^1$  represents  $N=CR^6R^7$  wherein

$R^6$  represents a hydrogen atom, methyl or optionally halogen substituted aryl, and

$R^7$  represents C1 - C4-alkyl or optionally halogen substituted aryl; or

$R^1$  represents an isonitrile, isocyanate, isothiocyanate or guanidino moiety.

Especially preferred are compounds of formula I1 – I13 wherein

$R^1$  represents  $NR^2R^3$  wherein

$R^2$  represents a hydrogen atom and

$R^3$  represents  $C=OR^4$  wherein

$R^4$  represents a hydrogen atom.

Especially preferred are also compounds of formula I1 – I13 wherein

$R^1$  represents  $NR^2R^3$  wherein

$R^2$  represents a hydrogen atom and

$R^3$  represents  $C=OR^4$  wherein

$R^4$  represents  $OR^5$  or  $NHR^5$  wherein

$R^5$  represents methyl, ethyl, n- or i-propyl or n-,s-,i- or t-butyl, or phenyl which is optionally substituted by halogen.

Especially preferred are also compounds of formula I1 – I13 wherein

$R^1$  represents  $N=CR^6R^7$  wherein

$R^6$  represents methyl, ethyl, n- or i-propyl, n-,s-,i- or t-butyl, or preferred a hydrogen atom or and

$R^7$  represents methyl, ethyl, n- or i-propyl, n-,s-,i- or t-butyl or phenyl.

Especially preferred are also compounds of formula I1 – I13 wherein

R<sup>1</sup> represents an isonitrile, isocyanate, isothiocyanate or guanidino moiety.

5 Preferred are compounds wherein n represents 1.

Preferred are compounds of the formula I8

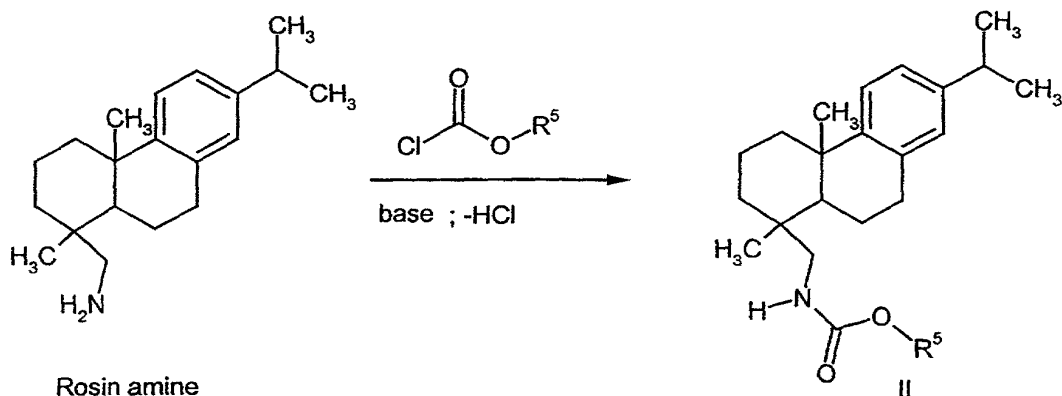
10 The aforementioned compounds are accessible by standard procedures of organic chemistry which can be adopted to the Rosin moiety. The starting Rosin derived from Tall Oil, Gum or Wood is commercially available; for example Rosin amine as Hercules® Amine D. An overview on the different isomers of abietic acid as well as their preparation is given by Gang-Fung Chen in *Progress in Organic Coatings* 20, 1992, 139-167. In the following general schemes the synthesis of the different Rosin  
15 amine derivatives is outlined. For reasons of simplification, the synthesis routes are outlined for substructure I8 with n = 1. The reaction sequences can be adopted easily to the other pure isomers and rosin oxidation/reduction products and also to mixtures of them.

20 **Scheme 1**

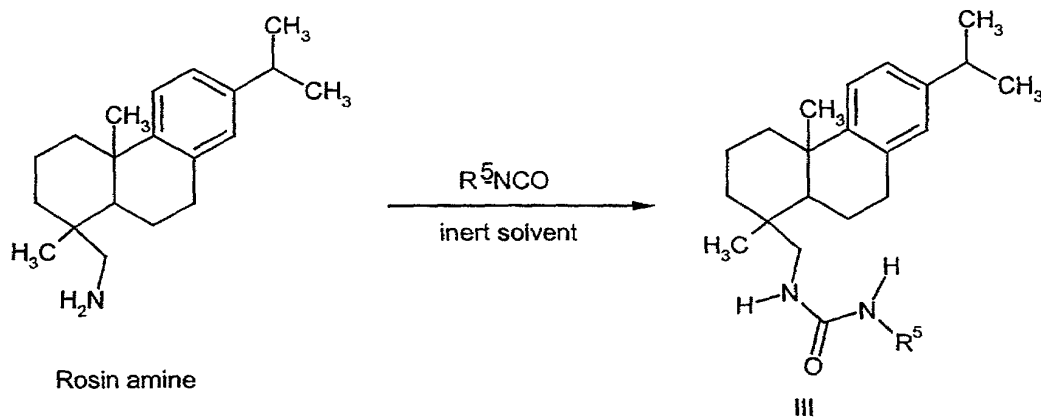
Compounds of formula I8 are accessible via acylation of Rosin amine with a chloroformic-ester in an inert solvent with a base as HCl acceptor (see: Houben-Weyl Vol.8, 1952, 137-140; ibid. Vol.11/2, 1958, 27-37).



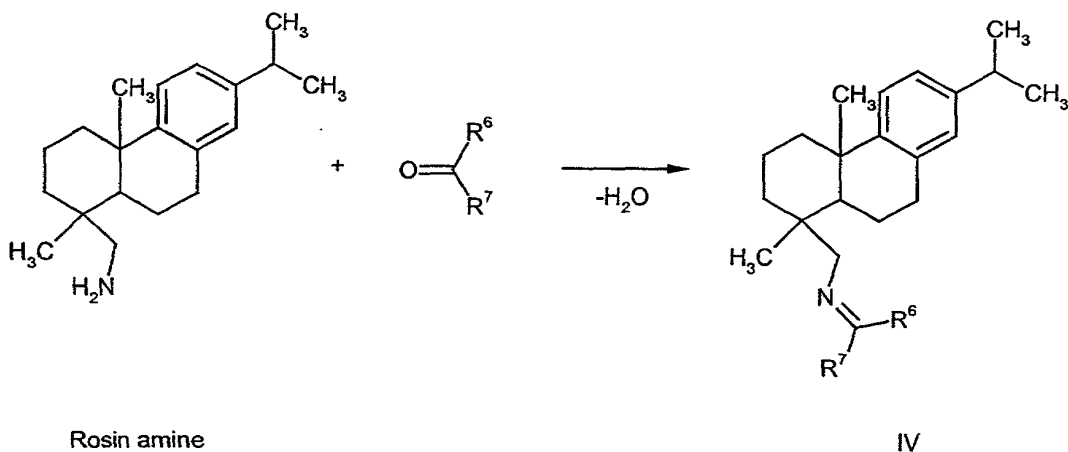
- 7 -

**Scheme 2**

Ureas of formula III can be synthesized by reacting Rosin amine with an isocyanate in an inert solvent (benzene, toluene, hydrocarbons etc.); see: Houben-Weyl Vol. E4, 1983, 352-357 or alternatively via reaction of Rosin isocyanate (s. below) with an aliphatic or aromatic amine.

**Scheme 3**

Schiff-bases of Rosin amine are accessible via condensation of Rosin amine with an aldehyde or keton (Houben-Weyl Vol. 11/2, 1958, 74-85).



The synthesis of Rosin isocyanide has been published (T. Ohsawa et al., Tetrahedron Lett., 1989, 845-846).

Rosin isothiocyanate (CAS-Nr.: 115 269-93-7) can be synthesized from Rosin amine through reaction with thiophosgene (see analogous sequence with phosgene: Ozaki, Chem Rev. 72, 457-460), or alternatively with a thiophosgene substitute, namely thiocarbonyl-diimidazole (see example 3).

The preparation of Rosin isocyanate has been described (E. Corey et al., Tetrahedron Lett. 1981, 299-302).

In the case of compounds of formula 1 with  $n = 0$ , the required starting material Dehydroabietan-1-yl-amine can be obtained according to Stockel et al., Can.J.Chem. 1963, 834-836.

The synthesis of Dehydroabietan-1-yl-isocyanate is described in Chem.Pharm.Bull. 1985, 1472-1487.

All other derivatives (formula I,  $n=0$ ) can be synthesized in analogous manner as described for Rosin amine.

### Detailed Description of the Preferred Embodiment

A fouling organism which may be combatted or controlled by the method of the invention can be any marine or freshwater organism which can attach to an inner or outer surface of a structure which is submerged or in continual contact with water.

5 Exemplary organisms include algae, including members of the phyla Chlorophyta, Phaeophyta and Rhodophyta; tunicates, including members of the class Ascidiacea such as *Ciona intestinalis*, *Diplosoma listerianum* and *Botryllus sclosseri*, and members of the class Hydrozoa including *Clava squamata*, *Hydractinia echinata*, *Obelia geniculata* and *Tubularia larynx*;

10 Bivalves including *Mytilus edulis*, *Cassostrea virginica*, *Ostrea edulis*, *ostrea chilensis*, *Lasaea rubra* and members of the family Dreissenidae (or zebra mussels) and members of the family Corbuculidae (or Asiatic clams), bryozoans including *Electra pilosa*, *Conopeum reticulatum*, *Bugula neritina* and *Bowerbankia gracilis*;

15 Polychaete worms including *Hydroides norvegica*, *Pomatoceros triqueter*, *Mercierella enigmata* and *Spirorbis spp.*;

20 Sponges and members of the class Cirripedia (barnacles) such as *Balanus amphitrite*, *Lepas anatifera*, *Balanus balanus*, *Balanus balanoides*, *Balanus hameri*, *Balanus creatus*, *Balanus improvisus*, *Balanus galeatus*, *Balanus eburneus*, *Elminius modestus*, *Balanus tulipiformis* and *Balanus perforatus*.

25 Organisms of the genus *Balanus* are frequent foulers of aquatic structures. Specific fouling organisms to which this invention is especially directed include barnacles, zebra mussels, algae, diatoms, hydroids, bryozoa, ascidians, tube worms and asiatic clams, but also the bacterial slime.

30 Among the aquatic structures which may be protected by the method of invention are any submerged or partially submerged structure, either mobile or stationary, such as

a fishnet, boat, ship, piling, cooling tower, pipeline, standpipe, heat exchanger, dam, intake screen or the like.

In actual practice compound of formula I1 – I13 may be brought into contact with a fouling organism by:

- coating the aquatic structure to be protected with an antifouling-effective amount of said Rosin Amine derivative such that the antifouling compound is released at the to be protected surface area into the aquatic environment immediately.
- including an antifouling-effective amount of the Rosin Amine Derivative within material formed into an aquatic structure which then releases said compound,
- releasing an antifouling-effective amount of said compound directly into the aquatic environment surrounding the structure to be protected,
- or any other method wherein the Rosin Amine Derivative comes in contact with the fouling organism.

The amount of Rosin Amine Derivative to be used in the method of invention will vary according to the specific compound used, the identity of the fouling organism to be controlled, degree of fouling pressure of the surrounding aquatic environment, the water temperature, the mode of contact and the like.

The Rosinamine derivatives can be used as individual active compounds or else in combination with active compounds usually employed in the anti-fouling sector. These can preferably be heavy metals, such as Cu, or heavy metal compounds, such as, for example, bis(trialkyltin) sulphides, tri-n-butyl laurate, tri-n-butyl chloride, copper(I) oxide, triethyltin chloride, tri-n-butyl(2-phenyl-4-chlorophenoxy)-tin, tri-

butyltin oxide, molybdenum disulfide, antimony oxide, polymeric butyl titanate, phenyl-(bispyridine)-bismuth chloride, tri-n-butyltin fluoride, manganese ethylene-bisdithiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate, the zinc salt or copper salt of 2-pyridinethiol-1-oxide, bisdimethyldithiocarbamoyl-  
5 zinc ethylenebisdithiocarbamate, zinc oxide, copper(I) ethylene-bis-dithiocarbamate, copper thiocyanate, copper naphthenate and tributyltin halides.

The action spectrum of the rosinamine derivatives is extended further or particular effects are achieved by these combinations of active compounds. Synergistic effects are obtained in many cases. The synergistic effect manifests itself particularly clearly  
10 if the active compound combinations are present in certain weight ratios. However, the weight ratios of the active compounds in the active compound combinations can vary within a relatively wide range.

Preferred combination partners for the rosinamine derivatives are algicides, such as diuron, dichlorophen, endothal, fentin acetate or quinoclamine, molluscicides, such as fentin acetate, metaldehyde, methiocarb, niclosamide, thiodicarb and trimethacarb, fungicides, such as dichlofluanid, tolylfluanid, iodopropargyl butylcarbamate, fluor-  
15 folpet and azoles, such as propiconazole, metconazole, cyproconazole and tebuconazole or conventional antifouling active compounds, such as 2-(N,N-dimethylthiocarbamoylthio)-5-nitrothiazyl, tetrabutyl-distannoxane, 2-tert-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, 2,4,5,6-tetrachloroisophthalodinitril, tetramethylthiuram disulphide, 2,4,6-trichlorophenylmaleimide, 2,3,5,6-tetrachloro-4-(methylsulphonyl)-pyridine, diiodomethyl-  
20 paratryl sulphone, thiabendazol, tetraphenyl-boron-pyridin salt, and the copper and sodium salt of 2-pyridinethiol-1-oxide.

The anti-fouling composition preferably comprises the rosinamine derivatives in concentrations of 0.5 to 60% by weight, preferably between 1 to 25% by weight.

Compositions of the invention comprise an aquatically acceptable inert carrier and an antifouling-effective amount of a Rosin Amine Derivative of formula I. For application onto structural surfaces, preferred compositions of the invention include a film-forming component such as a polymer resin solution. Exemplary polymer resins include unsaturated polyester resins formed from: a) unsaturated acids or anhydrides, such as maleic anhydride, fumaric acid, itaconic acid and the like; b) saturated acids or anhydrides, such as phthalic anhydride, isophthalic anhydride, terephthalic anhydride, tetrahydrophthalic anhydride, tetrahalophthalic anhydride, adipic acid, subacic acid, and the like; c) glycols, such as ethylene glycol, and the like; d) vinyl monomers, such as styrene, vinyl toluene, chlorostyrene, bromostyrene, acrylates like methylmethacrylate, ethylene glycol dimethacrylate and the like. Other suitable resins include vinyl ester-, vinyl acetate-, and vinyl chloride-based resins, elastomeric components, vulcanized rubbers, rosins, metalresinates and urethane-based resins.

For further description of components common in antifouling paints see Ungerer in Chem.Ind. 1985, 37, 730 – 732 and Williams in Antifouling Marine Coatings, Noyes, Park Ridge, 1973.

### Example 1

#### N-Formyl-rosinamine ( 1 )

The starting material Rosinamine (Hercules® Amine D) is a mixture of primary amines derived from modified Rosin. It is described as dehydroabietylamine of technical grade and was used in the following syntheses without further purification.

To a solution of Rosin amine in ethyl acetate 5 equiv. of ethyl formate are added at room temperature under continuous stirring. After 16h at rt, the solvent is evaporated to dryness and the residue is filtered through a short column of silica gel to furnish N-formyl rosin amine under the form of a compact resin (yield: 86%).

Characterisation: visqueous oil; <sup>1</sup>H-NMR, δ(ppm): 7.94-8.23(1H); 7.15 (1H); 6.99 (1H); 6.89 (1H); 5.46 (1H); 2.76-3.27 (5H); 1.22 (6H); 1.21 (3H); 0.95 (3H).

**Example 2****Rosin isocyanide ( 2 )**

Diisopropylamine (2.7 equiv.) and phosphorous oxychloride (1.1equiv.) were successively added dropwise to a stirred solution of N-formyl rosinamine in dichloromethane at 0°C under an atmosphere of dry nitrogen. After 1h at 0°C, a 20% solution of sodium carbonate was added and the reaction mixture was allowed to reach room temperature for 1h. 20% sodium carbonate and water were added, extraction of the aqueous phase with dichloromethane followed by filtration of the residue through a column of silica gel furnished Rosin isocyanide as a colourless oil (yield: 85%).

Characterisation: visqueous oil; <sup>1</sup>H NMR, δ(ppm): 7.16 (1H); 7.00 (1H); 6.88 (1H); 2.76-3.34 (5H); 1.22 (6H); 1.21 (3H); 0.98 (3H).

**Example 3****Rosin isothiocyanate ( 3 )**

A solution of thiocarbonyl diimidazole (1.5equiv.) in dichloromethane was added to a stirred solution of Rosinamine in dichloromethane at 0°C under an atmosphere of dry nitrogen. After the addition was complete, the reaction mixture was heated at 45°C during 16h. The solvent was evaporated and the solid residue filtered through a column of silica gel to furnish Rosinisothiocyanate as an oil (yield: 87%).

Characterisation: oil; <sup>1</sup>H-NMR, δ(ppm): 7.16 (1H); 6.99 (1H); 6.89 (1H); 3.37 (2H); 2.90 (2H); 2.82 (1H); 1.22 (6H); 1.21 (3H); 0.96 (3H).

**Evaluation of Marine Antifouling Activity of Test Compounds**

The rate of settlement of laboratory reared cyprid larvae of the barnacle *Balanus amphitrite* was determined for testing the activity of candidate anti-fouling compounds.

**Settlement Assay**

Tests are carried out in four replicates in sterile polystyrene multi well plates. Between 25 and 40 cyprid larvae are injected in the dishes containing either 2ml of

test solution (see below), solvent control or a positive control (Dichloro-n-octylisothiazolinone).

Dishes are incubated for 24h at a temperature of  $27^{\circ}\text{C} \pm 2$ . After incubation the cyprids are screened for signs of toxicity. Larvae are classified in three categories: A) alive and swimming; B) alive but not active; C) dead. The test is terminated by addition of a drop of 20% formaldehyde and the numbers of settled and non-settled larvae are counted.

Settlement is evaluated as follows: 1) Non settled: not attached free swimming cyprids; 2) settled cyprids: attached, but not metamorphosed cyprids; 3) barnacles: attached juvenile barnacles.

Categories 2 and 3 are considered to be settled. Percentage settlement in test solution is compared with controls. Estimates of the *median effect concentration* (EC-50) after 50 hrs. are calculated using the Spearman-Kärber method.

All seawater used is of natural origin and filtered unto 0.2 micron. Stock solutions of test compounds are prepared by dissolving an amount of test substance in a suitable solvent and subsequent addition of seawater.

The stock solutions are used to prepare several dilution series in seawater. Controls are made of seawater, or, if appropriate, in a mixture of seawater and solvent. The solvent concentration in the controls is equal to the highest concentration in the test solution. As an internal standard (positive control) a concentration range of 0 to 5ppm dichloro-n-octylisothiazolinone will is included in each test.

#### Test Results

Compound	EC50 for settlement inhibition in ppm
1	2.6

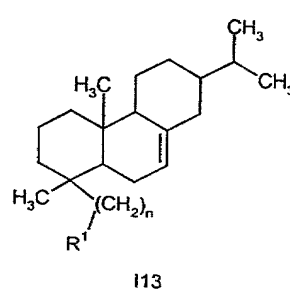
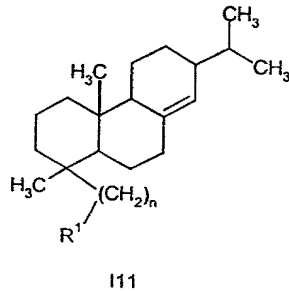
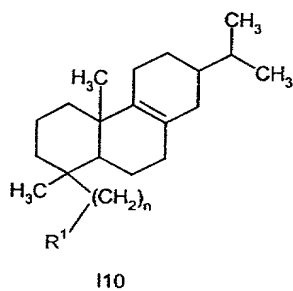
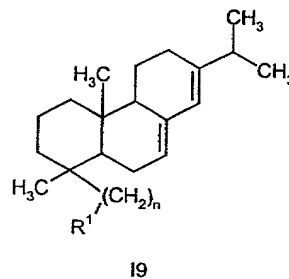
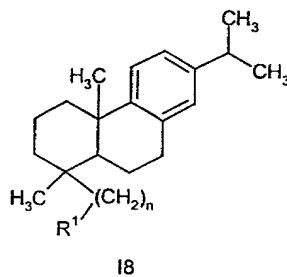
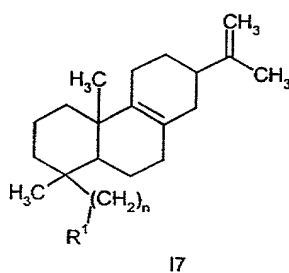
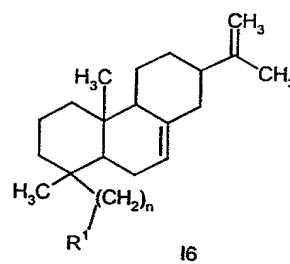
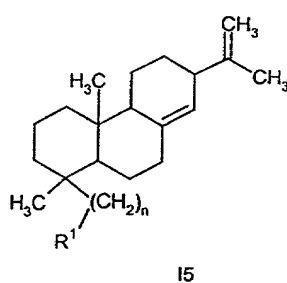
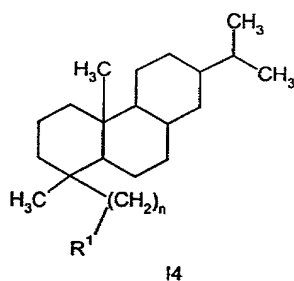
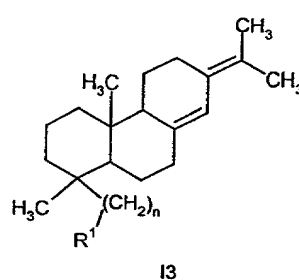
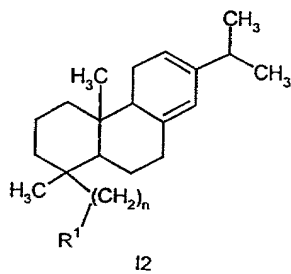
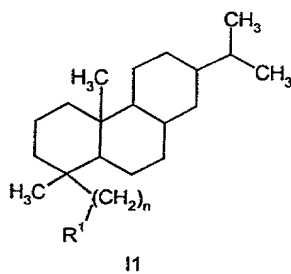


reference*	0.37
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\* ≡ 4,5-dichloro-n-octylisothiazolinone

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[illegible]

**PATENT CLAIMS****1. Compounds of the formula I**

wherein

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R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup> wherein  
R<sup>2</sup> represents a hydrogen atom, C1 - C8-alkyl and  
R<sup>3</sup> represents C=OR<sup>4</sup> wherein  
R<sup>4</sup> represents a hydrogen atom or one of the groups OR<sup>5</sup> or NHR<sup>5</sup>  
wherein  
R<sup>5</sup> designates C1 - C8alkyl or aryl, each optionally substituted by  
halogen; or

R<sup>1</sup> represents N=CR<sup>6</sup>R<sup>7</sup> wherein  
R<sup>6</sup> represents a hydrogen atom, C1 - C6-alkyl or aryl, and  
R<sup>7</sup> represents C1 - C6-alkyl or aryl, each optionally substituted by  
halogen; or

R<sup>1</sup> represents an isonitril, isocyanate, isothiocyanate or guanidino group;  
and

n represents 0 or 1.

2. Compounds of the formula I according to claim 1, wherein

R<sup>1</sup> represents NR<sup>2</sup>R<sup>3</sup> wherein  
R<sup>2</sup> represents a hydrogen atom or C1 - C4-alkyl and  
R<sup>3</sup> represents C=OR<sup>4</sup> wherein  
R<sup>4</sup> represents a hydrogen atom or one of the groups OR<sup>5</sup> or NHR<sup>5</sup>  
wherein  
R<sup>5</sup> represents C1 - C4-alkyl or aryl, each optionally substituted by  
halogen; or

R<sup>1</sup> represents N=CR<sup>6</sup>R<sup>7</sup> wherein  
R<sup>6</sup> represents a hydrogen atom, methyl or optionally halogen  
substituted aryl, and

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$R^7$  represents C1 - C4-alkyl or optionally halogen substituted aryl;  
or

$R^1$  represents an isonitrile, isocyanate, isothiocyanate or guanidino moiety.

3. Compounds of the formula I according to claim 1, wherein

$R^1$  represents  $NR^2R^3$  wherein

$R^2$  represents a hydrogen atom and

$R^3$  represents  $C=OR^4$  wherein

$R^4$  represents a hydrogen atom.

4. Method for controlling or combatting a marine or freshwater fouling organism which comprises contacting said organism or the locus thereof with an anti-fouling-effective amount of at least one compound of formula I as defined in claim 1.

5. Agents, characterized in that they comprise an antifouling-effective amount of at least one compound of formula I as defined in claim 1 and an aquatically acceptable inert carrier.

6. Use of compounds of formula I or agents as defined in claims 1 and 3 to control and combat marine and/or freshwater fouling organism.

7. Process for the preparation of anti-fouling agents, characterized in that compounds of formula I as defined in claim 1 are mixed with an aquatically acceptable inert carrier.

## COMBINED DECLARATION AND POWER OF ATTORNEY

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

**ROSIN AMINE ANTI-FOULING AGENTS**

the specification of which is attached hereto,

or was filed on **March 10, 2000**

as a PCT Application Serial No. **PCT/EP00/02118**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

**99 105 349.7**  
(Number)

**Europe**  
(Country)

**March 16, 1999**  
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Le A 33 210-US

HC

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and this application and to transact all business in the Patent and Trademark Office

JOSEPH C. GIL, Patent Office Registration Number 26,602 ARON PREIS, Patent Office Registration Number 29,426  
LYNDANNE M. WHALEN, Patent Office Registration Number 29,457 THOMAS W. ROY,  
Patent Office Registration Number 29,582 RICHARD E. L. HENDERSON, Patent Office Registration Number 31,619  
GODFRIED R. AKORLI, Patent Office Registration Number 28,779 N. DENISE BROWN, Patent Office  
Registration Number 36,097 NOLAND J. CHEUNG, Patent Office Registration Number 39,138  
DIDERICO VAN EYL, Patent Office Registration Number 38,641 CAROLYN M. SLOANE, Patent Office  
Registration Number 44,339 JAMES R. FRANKS, Patent Office Registration Number 42,552  
JACKIE ANN ZURCHER, Patent Office Registration Number 42,251  
RAYMOND J. HARMUTH, Patent Office Registration Number 33,896

all of Bayer Corporation, Pittsburgh, Pennsylvania 15205-9741

Send Correspondence To: Direct Telephone Calls To:

Patent Department

Bayer Corporation (412) 777-2349

100 Bayer Road

Pittsburgh, Pennsylvania 15205-9741

FULL NAME OF SOLE OR FIRST INVENTOR <u>Franz Kunisch</u>		INVENTOR'S SIGNATURE <u>Franz Kunisch</u>	DATE <u>2001-08-21</u>
RESIDENCE D 51519 <u>Odenthal</u> , Germany <u>DEX</u>		CITIZENSHIP German	
POST OFFICE ADDRESS c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany			
FULL NAME OF SECOND INVENTOR <u>Martin Kugler</u>		INVENTOR'S SIGNATURE <u>Martin Kugler</u>	DATE <u>2001-08-22</u>
RESIDENCE D 42799 <u>Leichlingen</u> , Germany <u>DEX</u>		CITIZENSHIP German	
POST OFFICE ADDRESS c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany			
FULL NAME OF THIRD INVENTOR <u>Jean-Claude Braekman</u>		INVENTOR'S SIGNATURE <u>Jean-Claude Braekman</u>	DATE <u>2001-08-20</u>
RESIDENCE B 1640 <u>Rhode Saint Genese</u> , Belgium <u>BEX</u>		CITIZENSHIP Belgian	
POST OFFICE ADDRESS 7 Av. Sainte Therese, B 1640 Rhode Saint Genese, Belgium			
FULL NAME OF FOURTH INVENTOR <u>Mark Plehiers</u>		INVENTOR'S SIGNATURE <u>Mark Plehiers</u>	DATE <u>2001-08-31</u>
RESIDENCE B 1000 <u>Bruxelles</u> , Belgium <u>DEX</u>		CITIZENSHIP Belgian	
POST OFFICE ADDRESS 21 Rue le Corregge, B 1000 Bruxelles, Belgium			
FULL NAME OF FIFTH INVENTOR <u>Gabriele Ferrari</u>		INVENTOR'S SIGNATURE <u>Gabriele Ferrari</u>	DATE <u>30-06-2001</u>
RESIDENCE NL 1780 AB <u>Den Helder</u> , Netherland <u>N/LX</u>		CITIZENSHIP Dutch <u>Italian</u>	
POST OFFICE ADDRESS Ambachtsweg 8A, NL 1780 AB Den Helder, Netherland			
FULL NAME OF SIXTH INVENTOR <u>Marcel Vos</u>		INVENTOR'S SIGNATURE <u>Marcel Vos</u>	DATE <u>31-08-2001</u>
RESIDENCE NL 1272HS <u>Huizen</u> , Netherland <u>N/LX</u>		CITIZENSHIP Dutch	
POST OFFICE ADDRESS Dr. Kuyperlaan 54, NL 1272HS Huizen, Netherland			
FULL NAME OF SEVENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			